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Coordination chemistry of alkali metals in a modified β-diketiminate ligand scaffold☆

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Dedicated to Prof. Robert Mulvey in celebration of his 65th birthday, with many thanks for all your support and encouragement.

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ABSTRACT

β-diketiminate (or NacNac) ligands are a widely used ligand class in the stabilisation of metal complexes across the periodic table, in part due to the ease of variability of the ligand steric and electronic effects either at the β-carbon atom or the *N*-Ar group. Functionalisation of the γ-carbon position is not typically observed however and examples of such complexes are scarce in the literature. Herein, we report on the synthesis and characterisation of alkali metal NacNac complexes which contain such γ-carbon functionalisation in the form of a methyl group. Deprotonation of the β-diketimine proligand ^{Me3Dip}NacNacH **1** (^{Me3Dip}NacNacH = $(CH_3)C(C(CH_3)NDip)_2H$, Dip = 2,6-*i*Pr_2-C_6H_3) by various alkali metal bases yielded the corresponding alkali metal complexes ^{Me3Dip}NacNacAM (where AM = Li **2**, Na **3**, K **4**, Rb **5**, Cs **6**) which have been fully characterised by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, while **3** and **4** have been structurally characterised by single-crystal X-ray diffraction. The solid-state structures obtained illustrate the varied range of coordination modes accessible to such group 1 metal complexes.

1. Introduction

Since their first reported use in the 1960s as stabilising ligands for homoleptic M(II) complexes (M = Co, Ni, Cu) [1–3], the β-diketiminate ligand class (also known as 'NacNac' due to their resemblance to the common 'acac' ligand) has been at the forefront in the stabilisation of low oxidation/coordination state metal complexes. [4,5] The relatively simplistic and high yielding synthesis of these monoanionic *N,N'*-chelating ligands, coupled with the ease of tuneability of the ligand steric and electronic factors [4], has facilitated the isolation of landmark metal complexes across the periodic table e.g. Jones and Stasch's magnesium(I) dimer **I** [6], Roesky's aluminium(I) **II** [7], Driess' silylene **III** [8] etc. (Fig. 1).

Functionalisation of the ligand system is most commonly achieved by modification of either the *N*-aryl groups or the R groups on the ligand backbone (Fig. 2). While typically regarded as spectator ligands, on occasion they have been observed to engage in unwanted side-reactivity due to the nucleophilic γ-carbon and the typically acidic R^1 groups on the β-carbon of the ligand backbone [9].

Although many variants have found extensive use in organometallic chemistry, the most commonly used *N*-Ar group is the 2,6-diisopropylphenyl (Dip) functional group [10], due to the increased steric protection it provides to the resulting metal centre. This particular NacNac (labelled as ^{Dip}NacNacH ($HC(C(CH_3)NDip)_2H$, Dip = 2,6-*i*Pr_2-C_6H_3)) does not typically include additional substitution at the *γ*-carbon position *i.e.,* anything greater in size than a proton. Functionalisation of this *γ*-carbon *i.e.,* with a methyl group to yield ^{Me3Dip}NacNacH **1** (^{Me3Dip}NacNacH = $(CH_3)C(C(CH_3)NDip)_2H$, Dip = 2,6-*i*Pr_2-C_6H_3) requires an additional synthetic step beyond the standard condensation route and has seen limited use as a result. Reported metal complexes of *γ*-carbon functionalised NacNac ligands are limited to Co [11], Pt [12,13], Al [14] and Fe. [15–20] In particular, the Holland group have found extensive use for these ligands in Fe chemistry e.g., to yield the bis-nitride Fe complex via reduction of dinitrogen, which upon treatment with acid produces ammonia. [15] To extend the chemistry of *γ*-carbon functionalised NacNac ligands, we herein describe the synthesis and isolation of a series of new alkali metal complexes via deprotonation of ^{Me3Dip}NacNacH **1** with a range of alkali metal bases.

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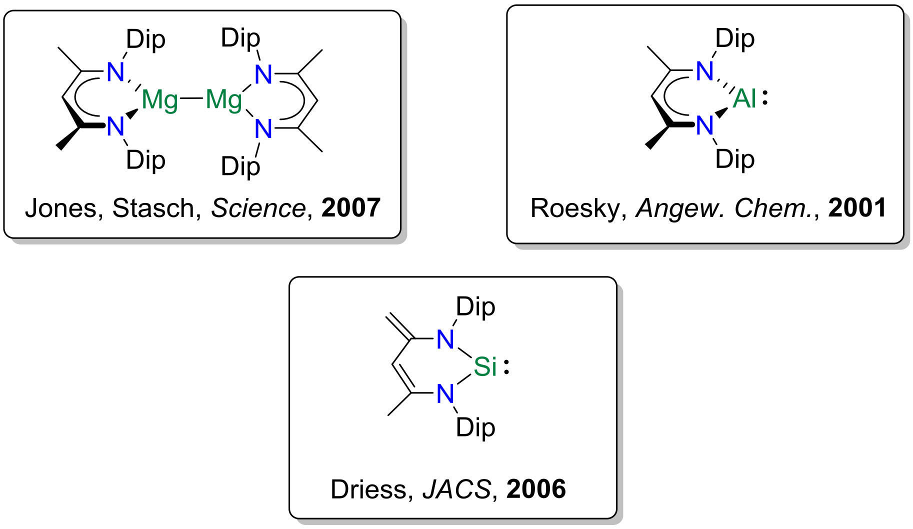


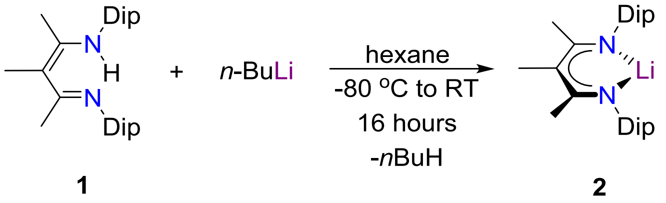
Fig. 1. Reported β-diketiminate stabilised low-oxidation state metal complexes (Dip = 2,6-diisopropylphenyl).

2. Results and discussion

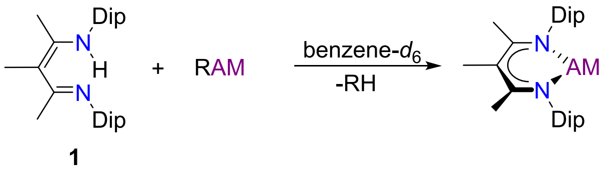
2.1. Synthesis and NMR spectroscopic analysis

Alkali metal salts of β-diketiminates are commonly used in main group chemistry due to their ease of synthesis and their ability to participate in salt-metathesis with a range of main group elements. [21] *n*-Butyllithium (*n*-BuLi), being the most commonly available strong alkali metal base, is regularly used to initiate the proligand deprotonation step to yield the desired lithium complex, which depending on the required reaction conditions can be carried out in either hydrocarbon or polar solvents at low temperatures (−78 °C). As expected, this method proved successful in the synthesis of $^{\text{Me3Dip}}$NacNacLi **2**, whereby addition of *n*-BuLi to a cooled hexane solution of $^{\text{Me3Dip}}$NacNacH followed by stirring at RT overnight precipitates **2** as a colourless powder in a yield of 52 % (Scheme 1). Subsequent analysis by ^{1}H NMR spectroscopy shows clean conversion of the β-diketimine proligand to the desired product indicated by the disappearance of the N—H resonance at δ 13.9 ppm. Analysis by ^{7}Li NMR spectroscopy also shows the presence of one lithium environment exhibiting a resonance at δ 0.76 ppm (*cf.* δ = −1.90 ppm for $^{\text{Dip}}$NacNacLi[10]).

Initial attempts to extend this to sodium using sodium bis(trimethylsilyl)amide (NaHMDS) required heating of the sample for an extended period, resulting in only approximately 50 % conversion after six days at 60 °C as judged by ^{1}H NMR spectroscopy (Scheme 2). Repeating using *n*-butylsodium (*n*-BuNa) in place of NaHMDS and following the reaction by ^{1}H NMR spectroscopy indicates approximately 60 % conversion to the desired sodium complex $^{\text{Me3Dip}}$NacNacNa **3** after only 20 min at RT, while almost quantitative conversion is observed after three hours. Scale-up attempts in toluene afforded **3** as a yellow crystalline solid in good yields (63 %) after work-up. The ^{1}H and ^{13}C {^{1}H} NMR spectrum of **3** is consistent with the proposed structural formulation.

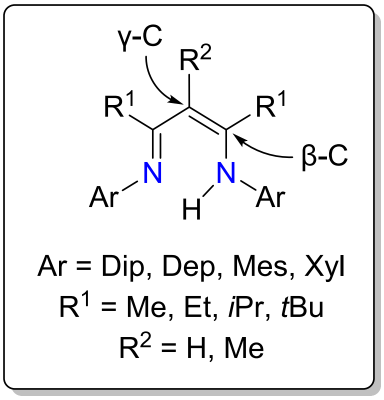


Scheme 1. Synthesis of $^{\text{Me3Dip}}$NacNacLi **2**.



For AM = Na (**3**); R = HMDS (60% conversion, RT, 6 days)
R = *n*Bu (>99 % conversion, RT, 16 hours)
For AM = K (**4**); R = HMDS (>99% conversion, 60°C, 5 days)
R = CH_2SiMe_3 (>99% conversion, RT, 16 hours)

Scheme 2. Synthesis of $^{\text{Me3Dip}}$NacNacNa **3** and $^{\text{Me3Dip}}$NacNacK **4**.

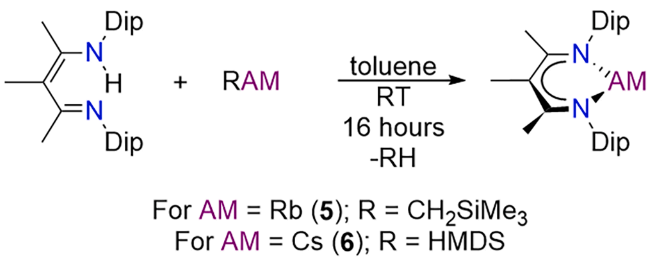


Ar = Dip, Dep, Mes, Xyl
R^1 = Me, Et, *i*Pr, *t*Bu
R^2 = H, Me

Fig. 2. Common Ar and R group variation in β-diketiminate ligands.

Similar extended reaction times and elevated temperatures were required for the synthesis of the potassium derivative via deprotonation of the ligand using potassium bis(trimethylsilyl)amide (KHMDS) – after five days of heating benzene-d_6 solutions of **1** and KHMDS to 60 °C almost quantitative conversion to $^{\text{Me3Dip}}$NacNacK **4** is obtained as judged by ^{1}H NMR spectroscopy. Subsequent attempts to synthesise **4** using KCH_2SiMe_3 required milder conditions and afforded almost quantitative formation of **4** after 16 h at RT (Scheme 2).

The rubidium derivative $^{\text{Me3Dip}}$NacNacRb **5** was subsequently



Scheme 3. Synthesis of ^{Me3Dip}NacNacRb **5** and ^{Me3Dip}NacNacCs **6**.

synthesised in analogous fashion to **4** using the corresponding $RbCH_2SiMe_3$ base, affording **5** in low yields (22 %) as a yellow crystalline solid, while ^{Me3Dip}NacNacCs **6** could be prepared via the reaction of caesium bis(trimethylsilyl)amide (CsHMDS) with **1** at ambient temperature in toluene overnight, in yields of 50 % (Scheme 3). Both **5** and **6** were fully characterised by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and are consistent with the expected structures of both.

No apparent trends were observed in the ^{1}H NMR spectra across the series of alkali metal complexes **2**–**6**. The spectra obtained display similar chemical environments to the respective (^{Dip}NacNac)M equivalent complexes e.g. **2** exhibits a multiplet in its ^{1}H NMR spectrum at δ 1.12–1.17 ppm for the Dip isopropyl CH_3 environment while (^{Dip}NacNac)Li exhibits the same environment between δ 1.12 and 1.16 ppm. In our experience, the ^{Me3Dip}NacNacM complexes show higher solubility in hydrocarbon solvents compared with the equivalent ^{Dip}NacNacM species.

2.2. *Crystal structures*

The molecular structures of **3** and **4** have been crystallographically characterised and show noticeably differing ligand–metal bonding modes. ^{Me3Dip}NacNacNa.C_7H_8 **3** crystallises as a monomeric species with two full molecules in the asymmetric unit, $Z' = 2$ (Fig. 3). Both sodium atoms are solvated by a single toluene molecule, exhibiting an asymmetric η^6 coordination mode and Na—C bond lengths ranging from 2.745(5) Å to 3.197(4) Å. Na—N bond lengths are consistent with previously reported NacNac sodium complexes (CSD-2079713 and CSD-2290068) [22,23] (Na2—N3: 2.267(3), Na2—N4: 2.264(3)), while the N—C (1.325(4) Å and 1.329(4) Å) and C—C (1.427(4) Å and 1.413(4) Å) bond lengths within the ligand are indicative of a delocalised system.

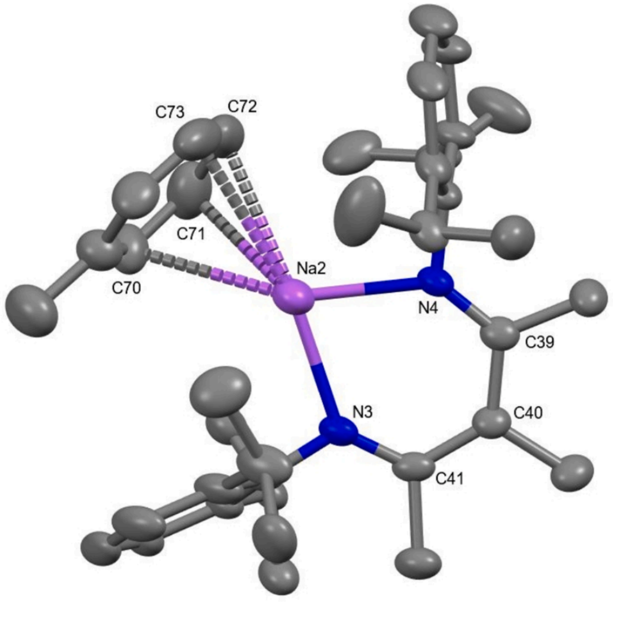


Fig. 3. Thermal ellipsoid plot (50 % probability level) of one of the crystallographically unique molecules of **3**.C_7H_8. Hydrogen atoms and minor disordered parts are omitted for clarity. Na-aryl interactions shown as dashed bonds. Selected bond lengths (Å) and angles (°): Molecule 1: Na1—N1 2.295(3), Na1—N2 2.279(3), Na1—C34 2.963(18), Na1—C35 2.912(7), Na1—C36 2.851 (6), Na1—C37 2.947(5); N1—C4 1.325(4), N2—C2 1.329(4), C2—C3 1.427(4), C3—C4 1.413(4); N1—Na1—N2 75.80(9); Molecule 2: Na2—N3 2.267(3), Na2—N4 2.264(3), Na2—C70 2.896(4), Na2—C71 2.745(5), Na2—C72 2.811 (5), Na2—C73 3.030(5); N3—C41 1.322(4), N4—C39 1.320(4), C39—C40 1.424(4), C40—C41 1.423(5); N3—Na2—N4 77.21(10).

The molecular structure of ^{Me3Dip}NacNacK **4** shows it to be a polymeric species (Fig. 4), similar to that of previously reported ^{Ar}NacNacK complexes. In the case of **4** however, the polymerisation is not solely achieved via η-coordination to the ligand aryl groups as is typically observed, but also through rotation of the NacNac ligand resulting in two different potassium environments. The first of these exhibits coordination to a nitrogen atom on two different NacNac ligands along with minor interactions with the *ipso*-carbon atom on the adjacent dip group. The second potassium centre is similarly bound to the other nitrogen atom on each of the NacNac ligands and shows additional coordination to both ipso- and *ortho*-carbon atoms on adjacent dip groups.

While the ligand system is twisted, the N—C (1.326(3) Å) and C—C (1.419(3) Å and 1.421(3) Å) bond lengths suggest a somewhat delocalised system similar to that present in **3**. The observed K-N bond lengths are consistent with those in previously reported NacNac potassium complexes. [24–27] This ligand rotation has previously been noted in related phosphorus complexes of **1**. [28].

3. Conclusions

In summary, a series of alkali metal complexes of the β-diketimine proligand ^{Me3Dip}NacNacH **1** have been synthesised by deprotonation using strong alkali metal bases e.g. *n*-butyllithium and *n*-butylsodium. Conversion of the proligand using AM-HMDS (AM = Na, K, Cs) bases typically required longer reaction times and/or elevated temperatures. Complexes **2**–**6** could be characterised by solution state NMR spectroscopy, while the solid-state structures of **3** and **4** were determined by X-ray crystallography. The structures of **3** and **4** show the unique range of coordination modes e.g. solvent/ligand arene interactions that can be accessed by such group 1 metal complexes. While pro-ligand **1** has been well established in Fe chemistry, its use in main group chemistry is still in its infancy. As such, the alkali metal complexes presented herein may aid the wider community to further explore and develop its potential applications.

4. Experimental

4.1. *General methods and instruments*

All alkali metal compounds described herein are highly air and moisture sensitive. As such all experimental work was carried out using standard Schlenk and glovebox techniques under a dry argon or dinitrogen atmosphere. Toluene, hexane and THF were collected from an Innovative Technology Solvent Purification System and stored over activated molecular sieves. Deuterated benzene was purchased from Sigma-Aldrich and stored over activated molecular sieves under argon. *n*-BuLi and sodium bis(trimethylsilyl)amide were purchased from Sigma-Aldrich and used as received. *n*-butylsodium [29], KCH_2SiMe_3, $RbCH_2SiMe_3$ [30], potassium bis(trimethylsilyl)amide [31] and caesium bis(trimethylsilyl)amide [32] were synthesised according to literature procedures. ^{Me3Dip}NacNacH **1** was synthesised using a modified literature method [15].

^{1}H, ^{13}C{^{1}H} and ^{7}Li NMR spectra were recorded on a Bruker AV3-400 spectrometer in deuterated benzene, operating at 400.4 MHz (^{1}H), 100.7 MHz (^{13}C{^{1}H}) and 155.5 MHz (^{7}Li), and were measured at 298 K. Chemical shifts were referenced to the residual ^{1}H or ^{13}C{^{1}H} solvent resonances or LiCl standard respectively. All chemical shifts are reported in ppm.

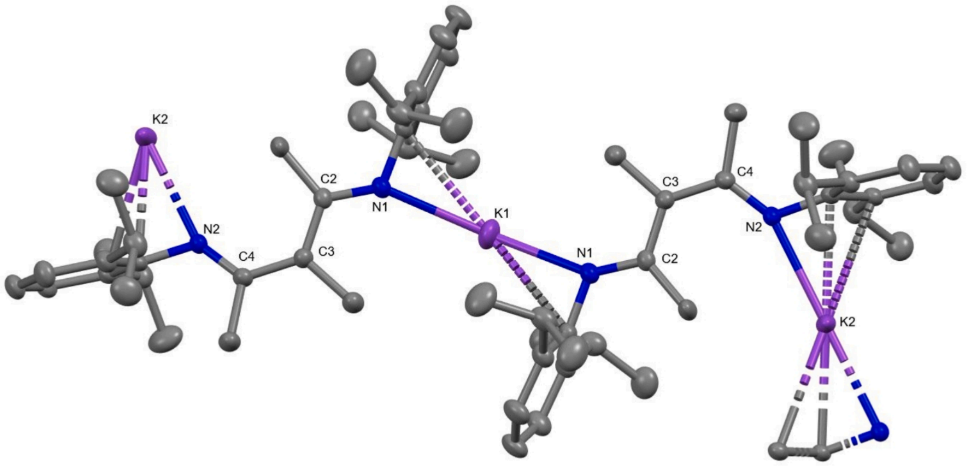


Fig. 4. Thermal ellipsoid plot (50 % probability level) of **4**. Hydrogen atoms and co-crystallised benzene molecule omitted for clarity. K-aryl interactions shown as dashed bonds. Selected bond lengths (Å) and angles (°): K1—N1 2.638(2), K2—N2 2.7131(19), N1—C2 1.326(3), N2—C4 1.326(3), C2—C3 1.419(3), C3—C4 1.421 (3); N1—K1—N1 150.53(10), N2—K2—N2 180(8).

Single crystal diffraction data for $\mathbf{3.C_7H_8}$ and **4** are reported in crystallographic information files (CIF) accompanying this document and deposited with the CCDC as deposition numbers **2409482** and **2409483**. Full details on data collection, reduction and refinement can be found in the individual CIFs. For $\mathbf{3.C_7H_8}$, a toluene ring of one unique molecule and two *i*-Pr groups of the other unique molecule were modelled as disordered. Appropriate constraints and restraints were applied to ensure that the displacement and geometric parameters of these groups approximated to normal behaviour.

4.2. Synthesis of *2*–*6*

4.2.1. ^{Me3Dip}NacNacLi (*2*)

$^{\mathrm{Me3Dip}}$NacNacH **1** (200 mg, 0.46 mmol) was dissolved in hexane (10 mL) and cooled to −80 °C. To this was added *n*-BuLi (0.35 mL, 0.55 mmol, 1.2 equiv.) dropwise and the solution was stirred for 30 min. This was then warmed to RT and subsequently stirred overnight. The resulting white precipitate was isolated by filtration and dried *in vacuo* to yield **2** as a white powder. Concentration of the filtrate to *ca.* 5 mL and storage at −30 °C for one day afforded a second crop of **2**. Repeated attempts to produce single crystals of **2** suitable for x-ray crystallographic analysis were unsuccessful. Yield = 105 mg (52 %).

^{1}H NMR: δ = 1.12–1.17 (m, 24H, Ar-CH(C*H*$_3$)$_2$), 1.93 (s, 6H, NC(C*H*$_3$)), 2.12 (s, 3H, NC(CH$_3$)C(C*H*$_3$)), 3.09 (sept, *J* = 6.9 Hz, 4H, Ar-C*H*(CH$_3$)$_2$), 7.12–7.19 (m, 6H, Ar-*H*).

^{13}C{^{1}H} NMR: δ = 18.9 (NC(CH$_3$)C(*C*H$_3$)), 22.2 (NC(*C*H$_3$)), 24.1 (Ar—CH(*C*H$_3$)$_2$), 24.2 (Ar—CH(*C*H$_3$)$_2$), 28.2 (Ar—*C*H(CH$_3$)$_2$), 123.0 (Ar—*C*), 123.5 (Ar—*C*), 140.9 (Ar—*C*), 149.9 (Ar—*C*), 163.4 (N*C*(CH$_3$)). The expected resonance for the backbone γ-carbon could not be observed.

^{7}Li NMR: δ = 0.76 ($^{\mathrm{Me3Dip}}$NacNac*Li*).

4.2.2. ^{Me3Dip}NacNacNa (*3*)

To a J. Youngs flask was added $^{\mathrm{Me3Dip}}$NacNacH **1** (100 mg, 0.23 mmol) and *n*-BuNa (24 mg, 0.300 mmol, 1.3 equiv.). Toluene (10 mL) was then added at RT and the resulting yellow solution was allowed to stir overnight. The solution was then concentrated *in vacuo* to approximately 5 mL and stored at −30 °C for two days to afford **3** as a yellow crystalline solid. Crystals suitable for X-ray crystallographic analysis were grown from a concentrated toluene solution of **3**. Yield = 63 mg (63 %).

^{1}H NMR: δ = 1.09 (d, *J* = 6.9 Hz, 12H, Ar—CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.9 Hz, 12H, Ar—CH(C*H*$_3$)$_2$), 1.96 (s, 6H, NC(C*H*$_3$)), 2.21 (s, 3H, NC(CH$_3$)C(C*H*$_3$)), 3.20 (sept, *J* = 6.9 Hz, 4H, Ar—C*H*(CH$_3$)$_2$), 7.03–7.07 (m, 2H, Ar—*H*), 7.14–7.17 (m, 4H, Ar—*H*).

^{13}C{^{1}H} NMR: δ = 19.2 (NC(CH$_3$)C(*C*H$_3$)), 22.2 (NC(*C*H$_3$)), 24.2 (Ar—CH(*C*H$_3$)$_2$), 24.4 (Ar—CH(*C*H$_3$)$_2$), 27.8 (Ar—*C*H(CH$_3$)$_2$), 91.1 (NC(CH$_3$)*C*(CH$_3$)), 121.3 (Ar—*C*), 123.5 (Ar—*C*), 139.8 (Ar—*C*), 150.9 (Ar—*C*), 162.0 (N*C*(CH$_3$)).

4.2.3. ^{Me3Dip}NacNacK (*4*)

To a J. Youngs flask was added $^{\mathrm{Me3Dip}}$NacNacH **1** (100 mg, 0.23 mmol) and KCH$_2$SiMe$_3$ (35 mg, 0.277 mmol, 1.2 equiv.). Toluene (10 mL) was then added at RT and the resulting red/orange solution was allowed to stir overnight. The solution was then concentrated *in vacuo* to approximately 5 mL and stored at −30 °C for two days to afford **4** as an orange crystalline solid. Crystals suitable for X-ray crystallographic analysis were grown from a concentrated benzene/hexane solution of **4**. Yield = 72 mg (72 %).

^{1}H NMR: δ = 1.03 (d, *J* = 6.9 Hz, 12H, Ar—CH(C*H*$_3$)$_2$), 1.23 (d, *J* = 6.9 Hz, 12H, Ar—CH(C*H*$_3$)$_2$), 2.03 (s, 6H, NC(C*H*$_3$)), 2.30 (s, 3H, NC(CH$_3$)C(C*H*$_3$)), 3.30 (sept, *J* = 6.9 Hz, 4H, Ar—C*H*(CH$_3$)$_2$), 6.98–7.02 (m, 2H, Ar—*H*), 7.13 (s, 2H, Ar—*H*), 7.15–7.16 (m, 4H, Ar—*H*).

^{13}C{^{1}H} NMR: δ = 18.9 (NC(CH$_3$)C(*C*H$_3$)), 22.4 (NC(*C*H$_3$)), 24.2 (Ar—CH(*C*H$_3$)$_2$), 24.3 (Ar—CH(*C*H$_3$)$_2$), 27.6 (Ar—*C*H(CH$_3$)$_2$), 120.5 (Ar—*C*), 123.8 (Ar—*C*), 139.4 (Ar—*C*), 150.9 (Ar—*C*), 159.8 (N*C*(CH$_3$)). The expected resonance for the backbone γ-carbon could not be observed.

4.2.4. ^{Me3Dip}NacNacRb (*5*)

To a J. Youngs flask was added $^{\mathrm{Me3Dip}}$NacNacH **1** (50 mg, 0.115 mmol) and RbCH$_2$SiMe$_3$ (24 mg, 0.138 mmol, 1.2 equiv.). Toluene (10 mL) was then added at RT and the resulting red/orange solution was allowed to stir overnight. The solution was then concentrated *in vacuo* to approximately 3 mL and stored at −30 °C for three days to afford **5** as a yellow/orange solid. Repeated attempts to produce single crystals of **5** suitable for X-ray crystallographic analysis were unsuccessful. Yield = 13 mg (22 %).

^{1}H NMR: δ = 1.06 (d, *J* = 6.9 Hz, 12H, Ar-CH(C*H*$_3$)$_2$), 1.22 (d, *J* = 6.9 Hz, 12H, Ar-CH(C*H*$_3$)$_2$), 2.06 (s, 6H, NC(C*H*$_3$)), 2.33 (s, 3H, NC(CH$_3$)C(C*H*$_3$)), 3.26 (sept, *J* = 6.9 Hz, 4H, Ar-C*H*(CH$_3$)$_2$), 6.98–7.14 (m, 4H, Ar-*H*).

^{13}C{^{1}H} NMR: δ = 19.4 (NC(CH$_3$)C(*C*H$_3$)), 22.6 (NC(*C*H$_3$)), 24.1 (Ar-CH(*C*H$_3$)$_2$), 24.2 (Ar-CH(*C*H$_3$)$_2$), 27.7 (Ar-*C*H(CH$_3$)$_2$), 92.8 (NC(CH$_3$)*C*(CH$_3$)), 120.7 (Ar-*C*), 123.8 (Ar-*C*),139.5 (Ar-*C*), 151.4 (Ar-*C*), 160.9 (N*C*(CH$_3$)).

4.2.5. ^{Me3Dip}NacNacCs (6)

To a J. Youngs flask was added ^{Me3Dip}NacNacH (50 mg, 0.115 mmol) and Cs(HMDS) (40 mg, 0.138 mmol, 1.2 equiv.). Toluene (10 mL) was then added at RT and the resulting red/orange solution was allowed to stir overnight. The solution was then concentrated *in vacuo* to approximately 1 mL and stored at −30 °C for three days to afford **6** as a dark orange solid. Repeated attempts to produce single crystals of **6** suitable for X-ray crystallographic analysis were unsuccessful. Yield = 33 mg (50 %).

^{1}H NMR: $\delta = 1.07$ (d, $J = 6.9$ Hz, 12H, Ar—CH(CH_3)$_2$), 1.22 (d, $J = 6.9$ Hz, 12H, Ar—CH(CH_3)$_2$), 2.09 (s, 6H, NC(CH_3)), 2.38 (s, 3H, NC(CH$_3$)C(CH_3)), 3.25 (sept, $J = 6.9$ Hz, 4H, Ar—CH(CH$_3$)$_2$), 6.98–7.14 (m, 4H, Ar—H).

^{13}C{^{1}H} NMR: $\delta = 20.4$ (NC(CH$_3$)C(CH$_3$)), 23.0 (NC(CH$_3$)), 24.2 (Ar—CH(CH$_3$)$_2$), 24.3 (Ar—CH(CH$_3$)$_2$), 27.7 (Ar—CH(CH$_3$)$_2$), 94.4 (NC(CH$_3$)C(CH$_3$)), 120.7 (Ar—C), 123.8 (Ar—C), 139.7 (Ar—C), 151.7 (Ar—C), 161.0 (NC(CH$_3$)).

CRediT authorship contribution statement

Stuart Burnett: Writing – original draft, Formal analysis, Data curation. **Alan R. Kennedy:** Writing – review & editing, Validation, Formal analysis. **Catherine E. Weetman:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2025.117461.

Data availability

CCDC **2409482** and **2409483** contains the supplementary crystallographic data for complexes **3** and **4**. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK; fax (+44)1223-336-033; ordeposit@ccdc.cam.ac.uk. The data that supports the findings of this study are available from the University of Strathclyde KnowledgeBase doi: 10.15129/4696f02c-59f6-48b9-830b-fe7c9717f92e. Supplementary data to this article can be found online.

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